6 Steam engines and refrigerators

6.1 The history of the steam engine

It was Denis PAPIN – the inventor of the pressure cooker, *cf.* Paragraph 2.4.8 – who first condensed vapor and lifted a weight by doing so. He used a brass tube of diameter 5 cm; some water at the bottom was evaporated and the vapor pushed a piston upward which was then fixed by a latch. Afterwards the tube was taken away from the fire, the vapor condensed and a Torricelli vacuum formed in the tube. When the latch was unlocked, the air pressure pushed the piston downward and lifted a weight of 60 pounds.

The first proper heat engine was constructed by Thomas NEWCOMEN (1663-1729), a blacksmith from Dartmouth in England. The Newcomen engines were used for pumping water out of coal mines. Fig. 6.1 shows a schematic picture of the engine: A movable piston closed off a cylinder and was pulled upward by a pump rod that turned a beam with two lateral arch heads. During the upward motion the cylinder was filled with steam at a pressure of 1bar. The entering steam pushed air and some water – left over from the previous stroke – out of the cylinder through an eduction pipe and a snifting valve. The piston was sealed with leather bands and water on top. After closing the steam valve a water cock was opened inside the steam-filled cylinder, whereupon the steam condensed and the piston came down, driven by the outside air pressure. The steam valve and the injection valve were controlled by a plug rod hanging down from the rotating beam.

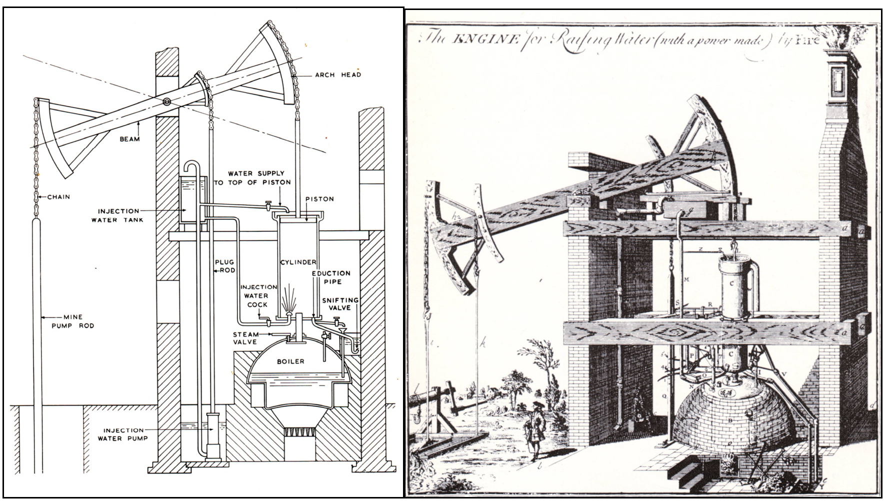


Fig. 6.1 Newcomen's steam engine (1712).

In the first Newcomen engine the cylinder had a diameter of 48 cm and the stroke of the piston had the length 1.80 m. In each downward stroke the piston lifted 40 l of water by 56 m, and the engine needed 5 s between successive strokes. It is easy to calculate that the power thus amounted to 4.5 kW. The engine was very reliable and by 1775 hundreds of them were installed, most of them in England and Scotland. The efficiency, however, was less than 1%:

*About 6 million of foot-pounds of useful work were done for each bushel of coal burnt.**

Because of the low efficiency James WATT (1763-1811) set himself the goal to improve the Newcomen engine. He was able to identify the reason for the low efficiency: Each batch of new steam had to reheat the cylinder walls which had just been cooled by the injected water. Thus a good part of the new steam condensed immediately. Therefore WATT had two objectives:

… first that the cylinder should be maintained as hot as the steam which entered it; and secondly, that when the steam was condensed, the water of which it was composed and the injection itself should be cooled as low as possible.

In pursuit of this program WATT invented the double-walled cylinder between whose walls the hot steam was conducted; and he invented the separate condenser. Fig. 6.2 shows WATT's steam engine of 1788.

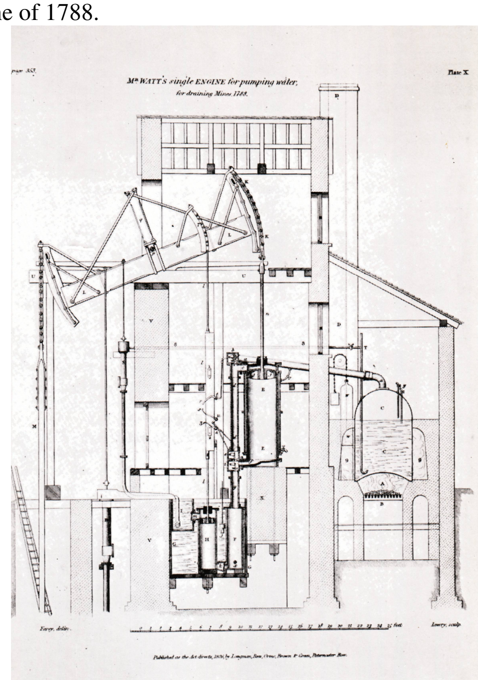


Fig. 6.2 WATT's steam pump to be employed in mines (1788).

Even WATT's earliest engines used only one third of the fuel compared to NECOMEN's. WATT and his partners allowed the engines to be built by their customers. They provided only the blueprints, valves and a supervisor, and as payment they asked for a part of the value of the fuel saved.

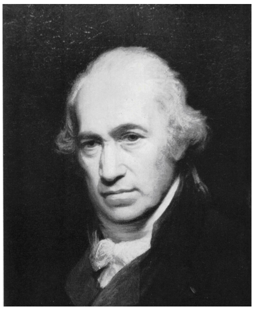
The use of high-pressure steam was delayed by the fear of exploding boilers. Pioneers of high pressure devices were the engineers Richard TREVITHICK (1771-1833) and Oliver EVANS (1755-1819). TREVITHICK also experimented with the possibility to close the steam

* R.J. Law. The steam engine. A Science Museum booklet. Her Majesty's Stationary Office, London (1965). Figs. 6.1 and 6.2 were taken from this brochure.

valve early during the working stroke and to let the steam expand afterwards. Thus less work was gained per stroke but still less steam was consumed so that the efficiency grew.

It is clear that when high pressure steam is employed, one does not need to have a low pressure in the condenser. Indeed, in this case one does not need a condenser at all: the expanded steam may simply be released from the cylinder into the atmosphere. Thus most steam locomotives do not have a condenser.

WATT has not only improved NEWCOMEN's engine, rather he has employed steam engines for many purposes other than pumping water out of mines. Thus in his "rotative engine" he has converted the up-and-down motion of the piston into the rotation of a wheel and a shaft. This engine has many uses: It could drive hammers, spinning wheels and looms, then ships and locomotives; in this manner WATT's inventions became the motor of the industrial revolution.



In 1783 WATT tested a strong horse and decided that it could raise a 150-pound weight nearly four feet in one second. He therefore defined a "horsepower" as 550 foot-pound per second. This unit is still in use. However, the unit of power in the international metric system is called one WATT. One horsepower equals 746 WATT.

6.2 Steam engines

6.2.1 *The (T,S)-diagram*

We recall Paragraph 4.1.1 where we have listed the advantages of the (T,S)-diagram for the evaluation of heats – added and withdrawn – and of the work of a cycle. Fig. 6.3 shows (T,S)-diagrams, on the left hand side a schematic one and on the right-hand side one for water and water vapor. In the latter case the entropy constant is arbitrarily chosen so that $S = 0$ holds in the triple point. This choice does not restrict the applicability of the diagram for the present purposes.

Inspection shows that the isobars in the vapor domain for high temperatures grow exponentially. This is the behavior expected for an ideal gas. In the liquid range all isobars up to 10^3bar are very close to the evaporation line.

6.2.2 *Clausius-Rankine process. The essential role of enthalpy*

Thermodynamically the cyclic process in the steam engine is identical to the Joule process that occurs in the hot air engine, *cf.* Paragraph 3.4.2, and which we have called the Joule cycle in that paragraph: Both cycles consist of two isobars and two adiabates. The difference is, of course, the working agent, steam instead of air. For the steam engine the cycle is called the Clausius-Rankine process. The individual branches of the cycle are as follows, *cf.* Fig. 6.4.

$2'$ - $3'$: The feed water pump compresses water adiabatically and feeds it into the boiler.

3′-3: In the boiler the water is isobarically heated to boiling and then evaporated; subsequently it may be superheated – still at a constant pressure – in the superheater.
3-2: In the steam cylinder the steam expands adiabatically.
2-2′: The steam is condensed in the cooler.

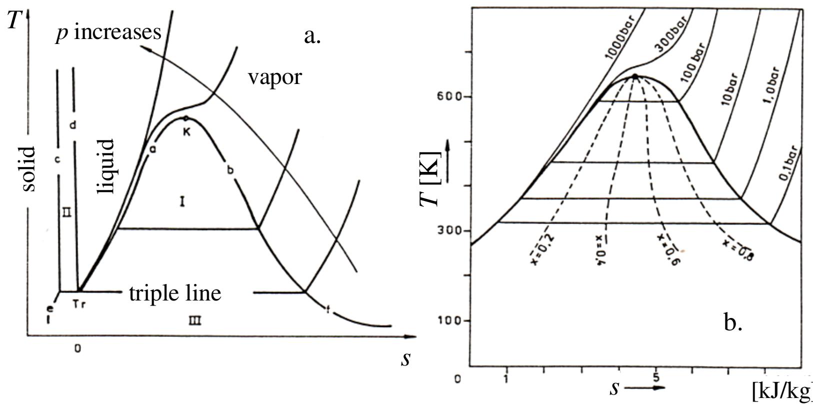


Fig. 6.3 a. (T,S)-diagram (schematic) Notation as in Fig. 2.7
b. (T,S)-diagram for water.

The elements of the hot air engine and of the steam engine correspond to each other as follows:

compressor	–	feed water pump
heat exchanger for heating	–	boiler and superheater
pneumatic engine	–	steam cylinder with piston
heat exchanger for cooling	–	condenser

Fig. 6.4 shows a schematic picture of the engine and also a standardized schematic picture in which the expansion occurs in a turbine rather than in the steam cylinder.

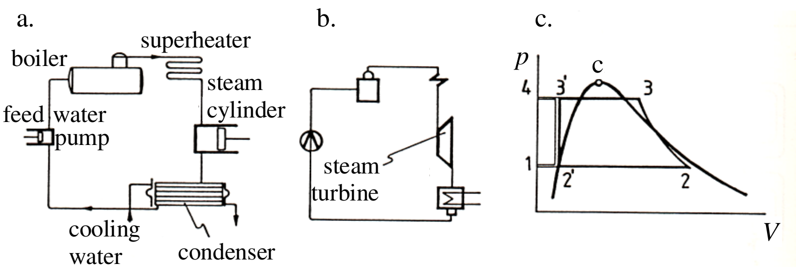


Fig. 6.4 a. Schematic picture of a steam engine
b. Standardized schematic picture
c. (p,V)-diagram with wet steam region.

The work of the feed-water pump and of the steam cylinder is represented in Fig. 6.4 by

$$W_{\text{FP}} = -\int_{12'3'4} p \, \mathrm{d}V \qquad W_{\text{FP}} = \int_{12'3'4} V \, \mathrm{d}p = \int_{2'}^{3'} V \, \mathrm{d}p$$
$$\text{or} \tag{6.1}$$
$$W_{\text{SC}} = -\int_{4321} p \, \mathrm{d}V \qquad W_{\text{SC}} = \int_{4321} V \, \mathrm{d}p = \int_{3}^{2} V \, \mathrm{d}p.$$

The last step in each line reflects the observation that $\mathrm{d}p = 0$ holds on the horizontal branches and that $V = 0$ on the branch 4-1. The branches $2'$-$3'$ and 2-3 are adiabatic. Therefore the First Law for reversible processes (1.57) reads

$$\dot{Q}\,\mathrm{d}t = \mathrm{d}U + p\,\mathrm{d}V = 0 \ , \text{ or with } \ H = U + pV : \ \dot{Q}\,\mathrm{d}t = \mathrm{d}H - V\,\mathrm{d}p = 0 \tag{6.2}$$

$V\,\mathrm{d}p$ may therefore be replaced in (6.1) by $\mathrm{d}H$ and we obtain

$$W_{\text{FP}} = H_{3'} - H_{2'} \text{ and } W_{\text{SC}} = H_2 - H_3 . \tag{6.3}$$

The total work of the cycle is then given by the difference of enthalpies

$$W = H_2 - H_3 - \left(H_{2'} - H_{3'}\right). \tag{6.4}$$

Equation $(6.3)_2$ states that the work of the steam cylinder is equal to the enthalpy drop of the steam. In Paragraph 1.5.9 we have seen that the work of a turbine is also determined by the enthalpy difference of the flow, *cf.* (1.80). This means that the thermodynamic treatment of the steam engine is unaffected, if the steam cylinder is replaced by a turbine: The amounts of work are equal.

For the work of the feed water pump we need not necessarily know the enthalpies of liquid water, as $(6.3)_1$ would suggest. Indeed, since water is to a good approximation incompressible, we have $V_{2'} \approx V_{3'}$. The area $(1, 2', 3', 4)$, which represents the work, may therefore be written as

$$W_{\text{FP}} = m\,\upsilon'(p_1)\left(p_4 - p_1\right), \tag{6.5}$$

where $\upsilon'(p_1)$ is the specific volume of liquid water at the lower pressure p_1, essentially $\upsilon'(p_1) \approx 1\ \text{l/kg}$.

Not only can the works involved in the operation of a steam engine be calculated from enthalpy differences, the same is true for the heats. Indeed, since the heating occurs on isobaric branches of the cycle we have

$$Q_{\text{boiler}} = H_3 - H_{3'} \quad \text{and} \quad Q_{\text{cooler}} = H_{2'} - H_2 .$$

6.2.3 *Clausius-Rankine process in a* (T, S)*-diagram*

Fig. 6.5 shows the Clausius-Rankine cycle in a (T, S)-diagram, with and without superheating, respectively. The individual branches represent

- 1-2: adiabatic compression in the feed-water pump.
- 2-3 (3′): isobaric heating and evaporation in the boiler (and superheating in a heat exchanger).
- 3-4 (3′-4′): adiabatic expansion, assumed reversible, *i.e.* isentropic.
- 4(4′)-1: condensation.

The distance of the isobar in the liquid region from the boiling line is exaggerated in Fig. 6.5; in reality, and on the scale of the figure, all isobars up to several

hundred bar virtually coincide with the boiling line, *cf.* Fig. 6.3. Therefore the graphs of Fig. 6.6 represent the cycle more realistically.

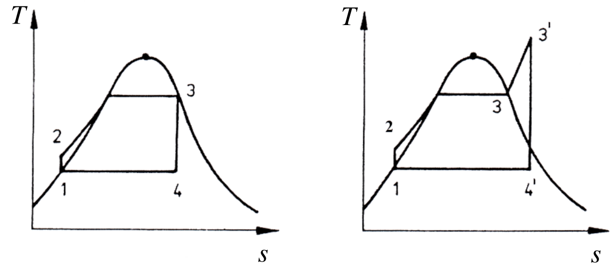


Fig. 6.5 (T,S)-diagram of the Clausius-Rankine process

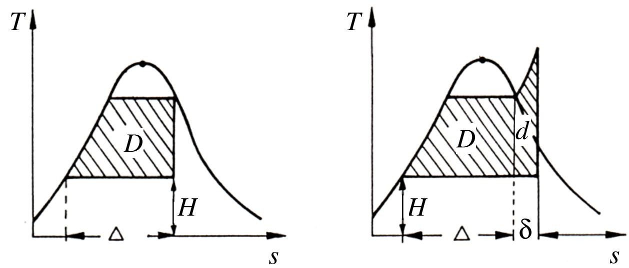


Fig. 6.6 The effect of superheating

As we already know, the (T,S)-diagram recommends itself by the fact that the area inside the process curve represents the work, while the areas below the upper and lower branches of the curve represent added and released heats, respectively. Therefore the efficiency of the process is easily visualized by a quotient of areas. For the cycles in Fig. 6.6 we have

$$e_{\text{left}} = \frac{D}{D + \Delta H} \quad \text{and} \quad e_{\text{right}} = \frac{D+d}{D+d+(\Delta+\delta)H} .$$

We may use this observation to prove that the efficiency of the process can be improved by superheating. We ask for the condition that $e_{\text{right}} > e_{\text{left}}$ holds and obtain after a short calculation

$$\frac{D}{\Delta} < \frac{d}{\delta} .$$

This means that the mean height of the quadrangle D must be smaller than that of the quadrangle d and this is indeed the case, since the isobars turn upwards after leaving the wet region.

Another practical reason for superheating – apart from increasing the efficiency – is that a full expansion downwards from point 3 to point 4, *cf.* Fig. 6.5 increases the moisture content at the end of the turbine, because point 4 lies deep in the wet steam region; this must be avoided, since water droplets may damage the turbine when hitting the blades.

On the other hand, superheating must not exceed 600°C, because this is a metallurgically safe temperature for the strength of the material of the superheater. Therefore it may be necessary to limit the superheating. In that case reheating after partial expansion may be employed in order to further prevent too much moisture in the turbine. The expansion is then split into two separate expansions that occur in a high pressure turbine and in a low pressure turbine. Between the turbines the partially expanded steam is lead through the boiler again where it is reheated to the boiler temperature, *cf.* Fig. 6.7.

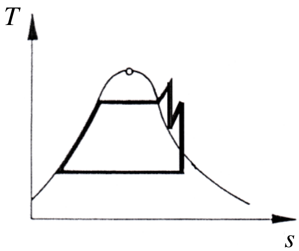


Fig. 6.7 Clausius-Rankine process with superheating and reheating to the boiler temperature

It is also clear that the expansion to a lower pressure will lead to more work, *cf.* Fig. 6.8. Of course, this measure is limited, because the pressure in the condenser cannot fall below the vapor pressure appropriate to the temperature of the cooling water. Also when the condenser pressure is too low, it becomes difficult to isolate the chamber and prevent the invasion of air.

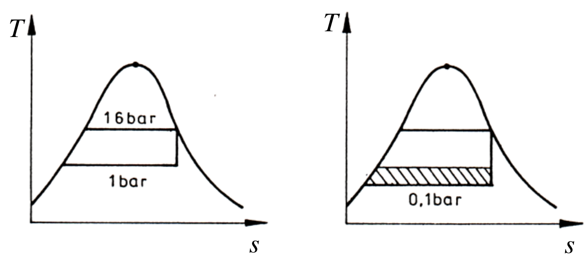


Fig. 6.8 Increase of work by lowering the pressure in the condenser

6.2.4 *The (h,s)-diagram*

The (h,s)-diagram is an important auxiliary tool in technical thermodynamics. It is often drawn so that the boiling line starts in the origin, which means that the additive constants in the entropy and in the enthalpy are both chosen as zero in the triple point. It is noteworthy that the isobars pass through the boiling line and through the dew line without a kink and that the slope of both lines is equal to T_C in the critical point. Fig. 6.9 a shows the (h,s)-diagram in schematic form, and with a cycle $123\,3'4'$ which represents the Clausius-Rankine process; once again

the distance of the isobar from the boiling point is exaggerated in order to be able to identify the adiabatic compression in the feed water pump.

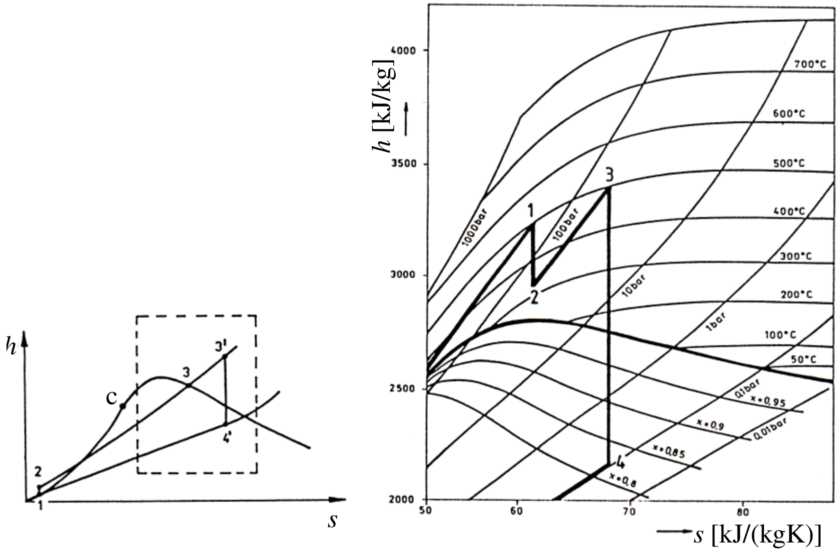


Fig. 6.9 a. Clausius-Rankine cycle in a (h,s)-diagram. Numbering as in Fig. 6.5
b. Relevant part of the (h,s)-diagram

In the (h,s) -diagram the works and heats needed for the calculation of efficiencies are easy to identify. Indeed, in Paragraph 6.2.2 we have shown that the works of the feed water pump and of the steam cylinder – or turbine -- are represented by enthalpy differences and so are the heats added or released in the boiler, superheater, and condenser. With the numbering of Fig. 6.9 a this means

$$\begin{array}{ll} w_{FP} = h_2 - h_1 & w_{SC} = h_{4'} - h_{3'} \\ q_+ = h_{3'} - h_2 & q_- = h_1 - h_2 \end{array}, \tag{6.6}$$

and the efficiency is given by

$$e = \frac{\left| h_{4'} - h_{3'} + h_2 - h_1 \right|}{h_{3'} - h_2}. \tag{6.7}$$

However, the diagrams used by engineers show only part of the full (h,s)-diagram. This part is indicated in Fig. 6.9 a by the dashed window. The information seen in this window suffices for efficiency calculations, although the points 1 and 2 are not shown. Indeed, h_1 may be calculated from Table 2.4 – with properties of boiling water and saturated steam – as $h'(p_4)$ and h_2 follows from

$$h_2 - h_1 = v'(p_{4'})(p_{3'} - p_{4'}) \tag{6.8}$$

for the work of the feed water pump, *cf.* $(6.3)_1$ and (6.5). $v'(p_{4'})$ may again be read off from Table 2.4.

6.2.5 *Steam flow rate and efficiency of a power station*

In a small power station, with a power output of 200 MW, steam of 500°C and 200 bar is fed into the turbine. The steam leaves the high pressure turbine at a pressure of 50 bar and is then reheated to 500°C by conducting it through a heat exchanger in the boiler. After that the steam is expanded in the low pressure turbine to the condenser pressure of 0.1 bar. The temperature rise of the cooling water for the condenser must be limited to ΔT_c=30 K.

The part of the process that is visible in a conventional (h,s) -diagram is represented in Fig. 6.9 b by the solid line. From this diagram we read off the specific enthalpies of the corner points*

$$h_1 = 3250\,\tfrac{\text{kJ}}{\text{kg}}\,,\; h_2 = 2900\,\tfrac{\text{kJ}}{\text{kg}}\,,\; h_3 = 3450\,\tfrac{\text{kJ}}{\text{kg}}\,,\; h_4 = 2150\,\tfrac{\text{kJ}}{\text{kg}}\,.$$

Hence follows the work of the two turbines

$$w_{\text{Tu}} = h_2 - h_1 + h_4 - h_3 = -1650\,\tfrac{\text{kJ}}{\text{kg}}\,.$$

The work of the feed water pump results from (6.8)

$$w_{\text{FP}} = v'(p_4)\,(p_1 - p_4) = 10^{-3}\,\tfrac{\text{m}^3}{\text{kg}}(200 - 0.1)\cdot 10^5\,\tfrac{\text{N}}{\text{m}^2} = 20\,\tfrac{\text{kJ}}{\text{kg}}\,.$$

$v'(p_4)$ must be taken from Table 2.4; its value is approximately $10^{-3}\,\tfrac{\text{m}^3}{\text{kg}}$, of course, irrespective of pressure. We see that w_{FP} is very small compared to the work of the turbines; it is often neglected in the calculation of the efficiency.

The heat supplied to the water and the steam in the boiler and in the heat exchangers for superheating and reheating is given by

$$q_+ = h_1 - \left[h'(p_4) + v'(p_4)(p_1 - p_4)\right] + h_3 - h_2 = 3590\,\tfrac{\text{kJ}}{\text{kg}}\,,$$

where $h'(p_4) = 190\,\tfrac{\text{kJ}}{\text{kg}}$ was read off from Table 2.4.

Thus the efficiency is given by

$$e = \frac{-w_{\text{Tu}} - w_{\text{FP}}}{q_+} = 0.46\,.$$

The mass flow of steam is

$$\dot{m}_{\text{S}} = \frac{200\,\text{MW}}{w_{\text{Tu}}} = 121\,\tfrac{\text{kg}}{\text{s}} = 436\,\tfrac{\text{t}}{\text{h}}\,.$$

The mass flow rate $\dot{m}_{\text{C}}$ of cooling water follows from the heat q_- to be absorbed in the condenser. We have

$$q_- = h_4 - h'(p_4) = 1960\,\tfrac{\text{kJ}}{\text{kg}}\,.$$

We set $\dot{m}_{\text{C}} c_{\text{W}} \Delta T_{\text{C}} = \dot{m}_{\text{S}} q_-$ where c_{W} is the specific heat of water and $\Delta T_{\text{C}} = 30\,\text{K}$ the temperature increase of the cooling water. Thus we obtain

$$\dot{m}_{\text{C}} = 1.9\,\tfrac{\text{t}}{\text{s}} = 6800\,\tfrac{\text{t}}{\text{h}}\,.$$

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* Students of technical thermodynamics are usually given a large-scale (h,s)-diagram which can be bought in university book stores, or they use electronic versions of the chart.

If the station were to work without reheating, the enthalpy of the steam after expansion from 200 bar to 0.1 bar would be equal to 1950 kJ/kg so that $w_{\mathrm{Tu}} = 1300\,\mathrm{kJ/kg}$. q_+ would be $3040\,\mathrm{kJ/kg}$ in this case and therefore e follows as 43% – instead of 46%. Therefore the reheating has improved the efficiency.

It is also interesting to compare these efficiencies with the efficiency of the Carnot engine working in the same temperature range between 500°C and $T(p_4) = 47°\mathrm{C}$. Such an engine would have the efficiency 59% according to (4.5) which would be the maximum that can be obtained for that temperature range.

6.2.6 *Carnotization*

We recall that the Carnot cycle has the largest efficiency among all cycles working in the same range of temperature. Also a reversible Carnot cycle – consisting of two isotherms and two isentropes – may be represented as a rectangle in a (T, s)-diagram, *cf.* Fig. 4.3. Having this in mind we consider again the Clausius-Rankine cycle – without superheating, *cf.* Fig. 6.10 a. This cycle is "nearly" a rectangle and one may ask why we do not make it into a Carnot cycle by stopping the condensation in the wet region at point 1 and pumping the wet steam into the boiler along the dashed isentrope. This, unfortunately, is impossible for practical reasons, because the wet steam – with its extreme differences of the density between boiling water and saturated steam – cannot be compressed in a pump without damaging the surface of a moving piston or of the turbine blades.

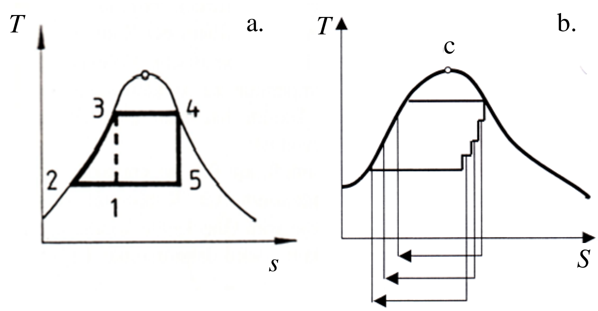

Fig. 6.10 Carnotization
a. An impossible proposition
b. Feed water preheating by partially expanded steam.

Another possibility for "Carnotization" of the Clausius-Rankine process is feasible, however: Before the water leaving the condenser is fed into the boiler by the feed water pump it is preheated in several steps, and the heat needed for this purpose is taken from the partially expanded – still hot – steam drawn from the turbine. Fig. 6.10 b shows, how the "heat packages" are transferred from the turbine to the feed water. The diagram in the figure is a (T,S)-diagram – not a (T,s) – so that with each withdrawal of steam the expansion isentrope moves to the left. If the steps are smoothed out, the cycle is represented by a parallelogram which has approximately the same area as the rectangle of Fig. 6.10 a. Thus the efficiency of the engine is that of a Carnot engine. Fig. 6.11 a shows how preheating the feed

water is realized in practice. After heat has been withdrawn from the steam it enters the condenser through a throttle valve. Up to six steps of preheating have been used.

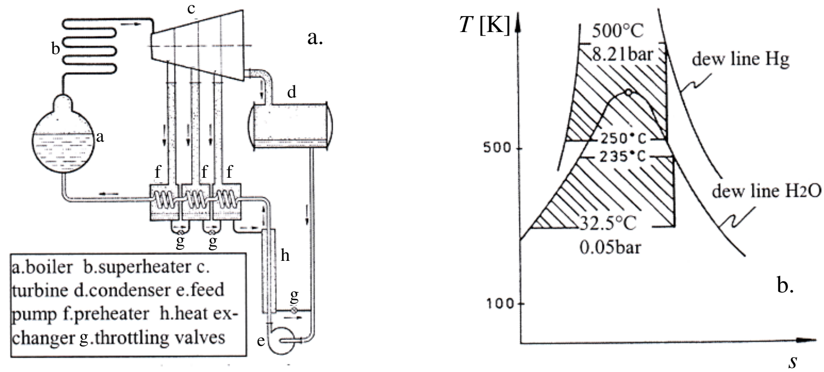

Fig. 6.11 a. Preheating feed water by partially expanded steam
b. Mercury-water cycle. The heat withdrawn from the mercury condenser is used to heat and evaporate water.

6.2.7 *Mercury-water binary vapor cycle*

Although the steam engine does not perform a Carnot cycle, its process curve is similar enough to that of a Carnot process that we may assume that a high temperature of the boiler is favorable for a large efficiency. Note that little, if anything, can be done about the temperature of the cooler; it is determined by the available cooling water which will generally be at environmental temperature.

In the case of water, however, high temperatures require high pressures. Therefore it has been proposed to use mercury as a working agent. Mercury has a critical temperature of 1460°C and a critical pressure of 1056 bar. However, at 500°C the vapor pressure is only 8.21 bar. On the other hand, at room temperature the vapor pressure is a minimal $3.6 \cdot 10^{-6}\,\mathrm{bar}$; accordingly the density is extremely small and a condenser at room temperature would thus be very large indeed in order to accommodate a reasonable mass flux. Also it cannot be effectively sealed without involving high costs.

In order to take advantage of the low vapor pressure at high temperature and still not be hampered by a large cooler volume, a hybrid mercury-water engine was constructed with a (T,s) -diagram as shown in Fig. 6.11 b: Mercury is evaporated at 500°C and 8.21 bar and expanded to 0.1 bar where the vapor temperature equals 250°C. The mercury condenser is cooled by water of $30.6\,\mathrm{bar}$ which evaporates at 235°C. Thus the mercury cooler acts as a boiler for the water cycle. The water steam is expanded to 0.05 bar, corresponding to 32.5°C.

The works of the mercury and the water cycles are shaded in Fig. 6.11 b. In an approximate manner the heat added is represented by the curve under the upper line of the mercury cycle so that even a cursory glance reveals that the efficiency of the combined engine is quite large.

Despite this the method is not practical, because in a pilot plant mercury was leaking everywhere; employees lost their hair and teeth and so the project was cancelled, although efficiencies higher than 50% had been reached.

6.2.8 *Combined gas-vapor cycle*

Progress in the construction of gas turbines involves water-cooled turbine blades and high-temperature-resistant coating of the blades with ceramic materials. Because of this, modern power plants – in the quest for high temperatures – make use of a combination of a Brayton cycle with air and of a Clausius-Rankine cycle in a steam engine.

Air may enter the compressor at 300K and – after compression, typically with a pressure ratio of 8:1 – it is heated isobarically by fuel combustion to temperatures of about 1300K. It is then expanded in a gas turbine and the exhaust gas of approximately 720K is used in the boiler of a steam engine to evaporate water and superheat it to 690K. The combined gas-vapor cycle is schematically shown in Fig. 6.12 and in the (T,s)-diagram of that figure.

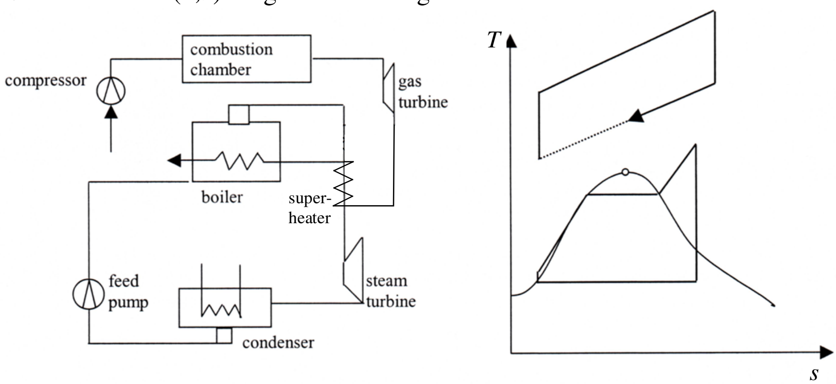

Fig 6.12 Combined gas-vapor cycle

6.3 Refrigerator and heat pump

6.3.1 *Compression refrigerator*

The cycle of a coolant in a compression refrigerator is in principle the inverse of the cycle of water in a steam engine. The purpose, however, is not the conversion of heat into work, rather it is the creation of cold by work. The most efficient way of producing cold is by evaporation; thus, if diethyl ether evaporates on the skin of the hand, the hand becomes cold, because the heat of evaporation is drawn from the skin, at least partly. This process requires no work; work is needed, however, when the cooling process is to be repeated over and over again.

In a refrigerator the refrigerant in the cooling coil boils and evaporates under small pressure and the necessary heat of evaporation is drawn from the food in storage (say). The saturated vapor is compressed – and heats up – isentropically in a compressor. Thus superheated vapor is created which is subsequently fed into a cooler – usually at the backside of the refrigerator – which may exchange heat with the surrounding air. The coolant condenses there and assumes room

temperature, still under a high pressure. Afterwards it expands through a throttling valve back into the low temperature boiler. The throttling is accompanied by partial evaporation and cooling. Fig. 6.13a shows the corresponding cycle in a (T,s)-diagram. The throttling step – indicated by the dashed line – is irreversible and increases the entropy.

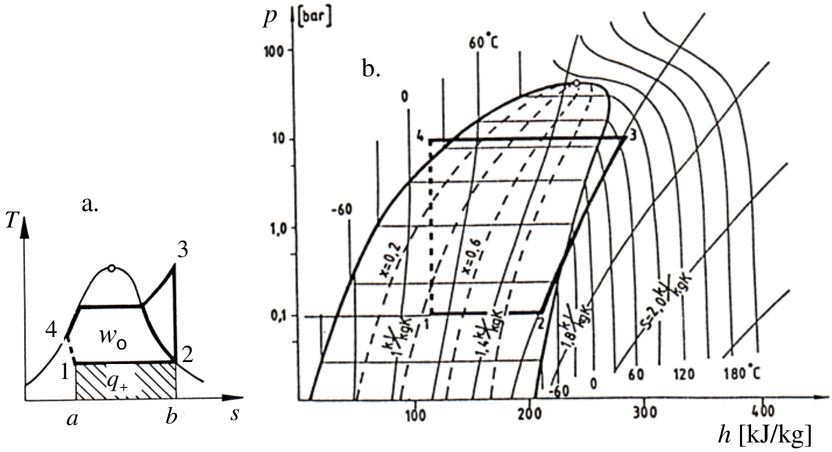

Fig. 6.13 a. Schematic cycle of refrigeration in the (T,s) -diagram
b. $(\log p, h)$-diagram of Freon12.

For a quantitative description of refrigerators the $(\log p, h)$ -diagram is useful. Fig. 6.13 b shows such a diagram for Freon12, a popular coolant. In the diagram the additive constants in entropy and enthalpy were arbitrarily chosen so that $s = 1\,\mathrm{kJ/(kgK)}$ and $h = 100\,\mathrm{kJ/kg}$ hold in the state where the coolant boils at 0°C. Detailed diagrams of this type are available in bookstores or in digitized version.

The efficiency of a thermodynamic machine is always the ratio of the desired output and the required input. However, output and input are radically different for the refrigerator and the steam engine. Indeed, the desired output in the present case is the heat q_+ withdrawn from the storage room and transferred to the coolant for evaporation. And the required input is the work w_0 needed for the operation of the compressor. In the (T,s) -diagram of Fig. 6.13 a both quantities are represented as areas and we have

$$e = \frac{q_+}{w_0} = \frac{\text{area}(a12b)}{\text{area}(1234)}.$$

Clearly the value of e may be larger than 1.

6.3.2 *Calculation for a cold storage room*

We investigate a refrigerator working with Freon12 that cools a storage room by withdrawing the heating $\dot{Q}_+ = 75\,\mathrm{kW}$. The coolant with the vapor content $x = 0.95$ and a pressure of $0.1\,\mathrm{bar}$ enters the compressor where the pressure is raised to 10 bar. The now superheated vapor is condensed and cooled to 20°C.

Finally by adiabatic throttling – at constant enthalpy – the coolant is expanded back into the boiler room at 0.1 bar.

The corresponding graphical cycle is shown in 6.13 b by a thick line and we read off:

boiler temperature: $-73°\mathrm{C}$, condenser temperature: $40°\mathrm{C}$.

The specific work of the compressor is equal to the difference of enthalpies before and after compression, see Paragraph 6.2.2. Thus we have, *cf.* Fig. 6.13 b

$$w_{\mathrm{o}} = h_3 - h_2 = (280 - 210)\tfrac{\mathrm{kJ}}{\mathrm{kg}} = 70\,\tfrac{\mathrm{kJ}}{\mathrm{kg}}\,.$$

The specific cooling is equal to the difference of enthalpies before and after evaporation

$$q_+ = h_2 - h_1 = (210 - 110)\tfrac{\mathrm{kJ}}{\mathrm{kg}} = 100\,\tfrac{\mathrm{kJ}}{\mathrm{kg}}\,.$$

Therefore we obtain the efficiency

$$e = \frac{q_+}{w_{\mathrm{o}}} = 1.43\,.$$

The rate of mass transfer is

$$\dot{m} = \frac{\dot{Q}_+}{q_+} = 0.75\frac{\mathrm{kJ}}{\mathrm{kg}} = 2.7\frac{\mathrm{t}}{\mathrm{h}}$$

and the power required for the compressor is

$$\dot{W} = \dot{m} w_{\mathrm{o}} = 52\,\mathrm{kW}\,.$$

6.3.3 *Absorption refrigerator*

Most of the parts of an absorption refrigerator are the same ones as those of a compression refrigerator. Thus in both cases there is an evaporator, a condenser and a throttling valve. However, the compressor is absent; the role of the compressor is played by the complex arrangement shown in Fig. 6.14 consisting of a cooled absorber, a pump, a heated generator, a rectifier and another throttling valve. Let us consider their functions, starting with the absorber which absorbs ammonia (say) coming from the evaporator of the plant – the place where the cold is generated by evaporation of ammonia under low pressure.

The ammonia vapor is absorbed by water, a reaction that is exothermic so that it releases heat. The mixture is cooled so that is may absorb more ammonia. It is then pumped to the generator where it is heated so as to produce an ammonia rich vapor. The pump serves to maintain the circulation. The pressure rises in the generator because of the evaporation of the NH_3-H_2O mixture. Thus the whole arrangement effectively works as a compressor. Water is split off the ammonia rich vapor in a rectifier so that essentially pure ammonia goes to the condenser. The hot and pressurized water runs back from the rectifier to the absorber through a throttling valve.

Absorption refrigerators were the first viable refrigerators in the 19th century before cheap electric motors were available for the compression of the evaporated gas.

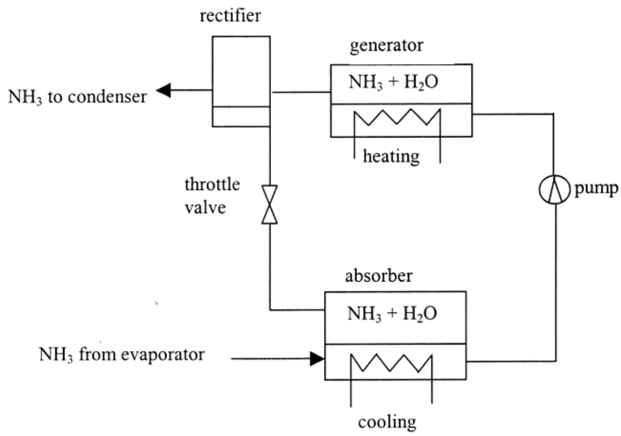

Fig. 6.14 Compression by desorption under heating in generator

6.3.4 *Refrigerants*

The coolant in a refrigerator cannot be water, since water freezes at small pressures near 0°C. The original and effective agent was ammonia NH_3, whose boiling point at 1bar is –34°C and, of course, for lower pressures it boils at even lower temperature. However, ammonia is not ideally suited, since – in the long run – it damages the pipes and the containers so that leaks will develop. In this respect fluorized hydrocarbons $C_kH_lCl_mF_n$ are better; these are usually known under commercial names, such as Freon, Frigen, Kaltron, *etc.*; they have recently acquired a bad reputation as “ozone killers.”

These gases are basically hydrocarbons of the form C_kH_{2k+2} – like methane CH_4, ethane C_2H_6, propane C_3H_8 – in which one or more hydrogen atoms are replaced by chlorine or fluorine, or both. In particular, the compounds with fluorine are very stable and, if fluorine atoms are involved, the chlorine atoms are also very strongly attached to the molecule. Therefore the compounds are chemically quite inert, *i.e.* they do not react, not even when heated.

Teflon is a long chain-molecule of that type and it is so stable that the coating of a frying pan survives the heat; nor does it combine chemically with the food broiled in the pan. Fluorized hydrocarbons were invented in the 1920s in the Dupont-Nemours laboratories, and the coolant Freon-11 (CCl_3F) and Freon-12 (CCl_2F_2) of this company are often used in refrigerators. It is said that, in the early days of marketing the chemicals, a Dupont agent took a deep breath of them and then, exhaling, he blew out a candle. Thus he demonstrated the chemical stability: The gas did not react, neither inside his lungs nor in the flame of the candle.

The scientific name of coolants is $R(k-1,l+1,n)$, where the “R” stands for “refrigerant.” Mono-chlorine-difluorine-methane $CHClF_2$ for instance is $R(22)$; it should be $R(022)$ but the initial zero is usually dropped. The three numbers k, l, n characterize the substance uniquely, since m is always equal to $2k+2-l-n$, because all C-bonds must be occupied.

Fluorized hydrocarbons – often mixtures of Freon-11 and Freon-12 – are frequently used as propellants in spray cans; at room temperature their vapor pressure is relatively small so that a thin and light aluminum can may serve as a safe container. In the end, of course all the industrially used freon ends up in the atmosphere and because of its stability it is not washed out by rain, nor does it combine with other substances that might form a sediment. So it diffuses throughout the air where it would seem to be innocuous, again because of its stability. However, in the upper atmosphere there *is* a process that can indeed shatter the molecules of the gas and will set the chlorine atoms free. That process is the bombardment of the molecules with high-energy ultraviolet radiation.

The lower atmosphere is shielded from the ultraviolet radiation of the sun by the stratospheric ozone layer which protects our skin from exposure to the high energy radiation. However, the ozone layer is slowly destroyed through reactions of the chlorine atom set free from a fluorized hydrocarbon. This atom reacts with ozone according to the chemical equation

$$\mathrm{Cl} + \mathrm{O}_3 \rightarrow \mathrm{ClO} + \mathrm{O}_2$$

and the chlorine oxide interacts with a rare O-atom to form O_2 and Cl again. The latter atom can again destroy an ozone molecule, *etc.* Thus even a small amount of freon in the atmosphere may be able to destroy a large amount of ozone and create the "ozone hole." As a result the damaging radiation can reach the organic molecules of plants and animals on the surface of the earth.

Therefore fluorized hydrocarbons were banned and it seems that in recent years the ozone hole is indeed becoming smaller.

6.3.5 *Heat pump*

Typically a heat pump is the same as a refrigerator. However, the purpose is different. While the required input is still the work of the compressor, the desired output is the cooling $|q_-|$ during condensation, *i.e.* the 3-4 branch in Fig. 6.13 a. In this case water may be used as the circulating agent, since usually all partial processes have temperatures above its freezing point.

The isobaric evaporation of water under low pressure – 0.1 bar (say) corresponding to a temperature of 7°C – may occur in pipes that are led through the groundwater. The condensation occurs in the living room which is to be heated. Recently an interesting variant was reported, where the evaporation took place in the cow-shed of a farm, while the condensation heated the living quarters.

The efficiency is given by

$$e = \frac{|q_-|}{w_0} = \frac{w_0 + q_+}{w_0},$$

where q_+ is the heat added to the process for the evaporation of the water. It is thus obvious that the efficiency of a heat pump is always greater than one.

We consider a heat pump working with Freon-12 so that we may use the diagram of Fig. 6.13b. Wet vapor is evaporated and superheated at 1.5 bar until it reaches a temperature of 45°C. Then follows the compression. The subsequent

cooling and condensation proceeds until the coolant is fully liquid at 30°C. The process is closed by throttling. The required heating $|\dot{Q}_-|$ is 10^3 kW .

The cycle is represented in Fig. 6.15 by the thick lines. We read off all relevant data of the process as follows.

- temperature after compression: 105°C
- pressure ratio of compressor: $\frac{8}{1.5} = 5.3$
- specific work of the compressor: $w_o = h_3 - h_2 = 40\,\frac{\text{kJ}}{\text{kg}}$
- specific heat gained: $|q_-| = h_3 - h_4 = 185\,\frac{\text{kJ}}{\text{kg}}$
- efficiency: $e = 4.6$
- mass transfer: $\dot{m} = \frac{|\dot{Q}_-|}{|q_-|} = 5.5\,\frac{\text{kg}}{\text{s}} = 19.5\,\frac{\text{t}}{\text{h}}$
- power of compressor: $\dot{W} = \dot{m}\,w_o = 216\,\text{kW}$.

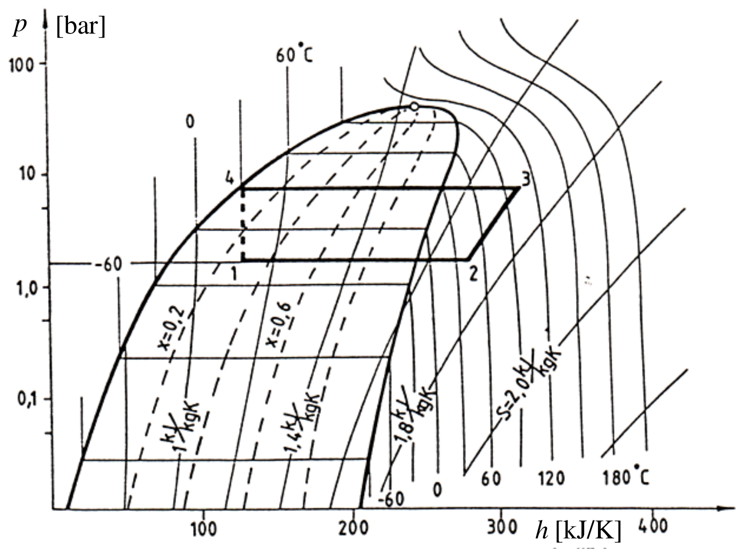

Fig. 6.15 On the layout of a heat pump